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Modelling sorption of ciprofloxacin using the ASM-X framework – Evaluation of factors influencing activated sludge treatment and implications on environmental risk assessment

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This abstract is meant as Platform presentation

Ciprofloxacin is a broad-spectrum antibiotic widely used in several anti-bacterial therapies. It was found to be toxic to the cyanobacterium *M. aeruginosa* at concentrations in the low µg/L range ([1], [2]), and a risk assessment study identified ciprofloxacin as potential environmental concern in Norway ([3]). Other investigations suggested the potential for ciprofloxacin to develop resistance in pathogens ([4], [5]). As a zwitterionic chemical, solid-liquid partitioning of ciprofloxacin is impacted by pH conditions and ionic interactions in solution [6]. In full-scale activated sludge systems, potential factors influencing the sorption of ciprofloxacin were identified as complexation with metal salts dosed for chemical phosphorus removal and specific pH conditions in anoxic and aerobic reactors [7]. The removal of ciprofloxacin in a full-scale wastewater treatment plant (WWTP) – Bekkelaget WWTP in Oslo, Norway – was assessed with the activated sludge modelling framework model for xenobiotics (ASM-X), a mechanistic model aiming to predict the fate of trace chemicals in activated sludge systems ([7], [8]). However, a systematic discrepancy between simulation results and measured data was exhibited, the latter showing a reduced removal of the substance in both anoxic and aerobic activated sludge reactors. A potential cause was identified in a deterioration of sorption as removal mechanism of dissolved contaminant from the sewage stream. The partitioning kinetics of ciprofloxacin was therefore investigated, and two alternative submodels were included in ASM-X and evaluated: (i) the already tested linear sorption – based on the partitioning coefficient K_D – ([7], [8]); and (ii) Freundlich-based exponential sorption rate.

Targeted batch sorption experiments were performed at different pH values (3.0, 6.3, 7.4, 8.0, 12.0) and iron salt dosing conditions (Fe(II) or Fe(III) salts used for chemical phosphorus removal) and Freundlich isotherms were obtained for each case, as reported in [9]. The Freundlich-based submodel for sorption was included in an extended version of ASM-X, thereby increasing the complexity of the model. Experimentally derived values for Freundlich parameters – Freundlich capacity factor (K) and intensity parameter (1/n) – were included in the model and full-scale predictions of aqueous concentration of ciprofloxacin were tested against data measured in a 3-day

campaign. Prediction accuracy by ASM-X employing the linear sorption submodel and extended ASM-X was statistically evaluated. Concentrations of ciprofloxacin in the effluent, as estimated by ASM-X, were used for a preliminary environmental risk assessment. Effluent predicted environmental concentrations ($PEC_{effluent}$) were estimated using a reported dilution factor for Oslofjord [10]. Risk quotients were calculated based on PNEC values reported by [3].

Comparison of full-scale outputs from extended ASM-X and measured concentration data indicate that sorption is likely to be reduced due to the effect of pH in activated sludge reactors. Most accurate prediction were obtained for K=0.01 ($\mu g^{(1-1/n)}$ $L^{1/n}$ mg^{-1}) and 1/n=1.33 Particularly, pH increase was estimated to cause reduced sorption in anoxic and aerobic reactors, as a consequence of the speciation of ciprofloxacin [6]. This is in agreement with recent findings that anionic species adsorb to a much lesser extent than cationic species [11]. Salt dosing conditions were estimated not to have any specific effect on sorption. Reliable full-scale predictions were obtained also using linear sorption, therefore indicating comparable prediction goodness at both model complexity levels assessed. As a result of a preliminary calibration, anoxic and aerobic K_D values were estimated to 1.1 and 0.42 L gX_{SS}^{-1}, respectively. These values were estimated to be reduced by a factor of 20 when deteriorated removal of ciprofloxacin was registered. Using the first and second lowest PNEC value reported by [3], the 8-hour median $PEC_{effluent}$ obtained are 454 – 1304 ng/L, resulting in risk quotients of 27 – 260. Relevant potential risk can be consequently associated to ciprofloxacin at local level.

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